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DISPOSAL OF TEXTILE INDUSTRY WASTEWATERS

This paper is a review of to-date research work on the treatment of textile industry wastewater with application of mechanical, physicochemical, chemical and biological methods. Also, technological systems in operation and suggested for application in textile industry wastewater treatment have been presented. On the basis of results obtained by various researchers a simple method of post-dyeing wastewater treatment applicable to all dyes and supported with author's own analysis of phenomena occurring in the process of dyes removal has been proposed.

1. INTRODUCTION

In production processes of textile factories considerable volumes of wastewater are generated particularly when wet treatment of fibre takes place. Composition of textile industry wastewaters is diverse and depends on: technological operations, type of raw material and dyes being applied. The most difficult to treat are post-dyeing wastewaters generated in dyeing of fibre and fabric processes. They comprise some dyes which are very difficult to remove because of complexity of their chemical composition.

In most cases, the post-dyeing wastewater is directed to a biological effluent treatment plant and often after biological treatment it does not change colour or its discolouration is insignificant. Therefore, it is necessary to get rid of dyes before effluents are subjected to the biological treatment stage. Many methods of effluents discolouration and purification have been developed so far but they are expensive to run, not very efficient and work only in the case of some selected dyes. Therefore, the objective of this paper is to propose, on the grounds of research work being carried out to date, a simple and universal method applicable to effluents containing various dyes and to draw up some assumptions and a research work plan for the method proposed to be verified.

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2. RESEARCH ON THE TREATMENT OF TEXTILE INDUSTRY WASTEWATERS

The biological method is a universal method of wastewater treatment and the more averaged the effluent and the more steady its supply to the activated sludge devices, the more efficient the method is. Often application of biological treatment exclusively to textile industry wastewaters poses difficulties due to lack of proper nutrient substances necessary for bacterial flora development. Therefore, textile industry effluents should be mixed with domestic sewage before being directed to biological treatment. According to LASKOW [1] valuable results can be obtained if 1:1 wastewater mix ratio is applied. Some research work having been done in England showed that it is necessary to add nutrient medium to wastewater in amount of 30 mg N/dm^3 and 6 mg P/dm^3 [2] during running-in of the activated sludge. In the USA, it is considered that cotton industry wastewaters treated by the activated sludge method should be clarified in full oxidation process, i.e., with prolonged aeration.

During treatment of wool both fat and sweat get into the wastewater. Both fat and sweat are easily biodegradable [3]. Wool sweat comprises potassium salts which can contribute, in the case of some wool sweats, up to 3.5% of mass, therefore, their concentration can be quite high whilst that of phosphates can be insufficient [4]. Furthermore, wastewaters generated in wool processing can contain considerable amount of sodium chloride – up to 20 g/dm^3 [5].

Particularly difficult to remove from textile industry wastewaters are dyes which are often bacteriostatic. For example, basic aniline dyes like gentian violet, methyl violet, malachite green, fuchsine and other retard development of Gram-positive bacteria having weaker influence on the Gram-negative ones. Other dyes like, e.g., acridine ones (acriflavine, proflavine and other) simply kill bacteria. Therefore, there is a maximum admissible concentration of dyes at which the process of wastewater biodegradation runs properly [1]. LASKOW showed that acid dyes with concentrations below 25 mg/dm^3 are fully degradable [1]. Other researchers [6] have determined maximum admissible concentrations for:

Congo dye – 25 mg/dm^3,
Diazo Blue – 120 mg/dm^3,
Direct Brown – 60 mg/dm^3,
Direct Black – 60 mg/dm^3 .

For vat and sulfur dyes the maximum admissible concentration has been determined at the level of 400 mg/dm^3 [7]. DOWNING [8], who was investigating the influence of methylene blue on nitrification, found that the dye had detrimental effect with its dose being over 100 mg/dm^3. American researchers [9], whilst carrying out investigations with application of the activated sludge to model solutions of 18 dyes, have succeeded in biodegradation of 3 dyes, 4 dyes have been precipitated and 11 stayed intact in the solution. On the other hand, HEUKELAINEN [9] considered that dyes were not subject to biodegradation and decrease of colour intensity was due to their adsorption on the activated sludge. ALEKCEEV [10], having investigated real textile industry wastewaters, showed that it was possible to have 30–50% colour intensity reduction because of dye adsorption on the activated sludge.

Research carried out on the model solutions of Black Acid D and Direct Acid Black Z [1] showed that even with dyes concentration of 0.3–0.5 mg/dm^3 the process of biodegradation was being ceased. Increase of dyes concentration up to 10–50 mg/dm^3 resulted in a strong inhibition of nitrification. Also the authoress of this paper investigated biodegradation of dyes [11], [12]. In her work, she showed that the activated sludge adapts very well to Helactine Scarlet D2GE and maintains 80% of its activity with the dye dose amounting to 79 mg/dm^3. The dye easily adsorbs on the activated sludge causing that the intensity of its colour increases with an increase of the dye concentration. However, despite of over eighty days of adaptation, the biodegradation of the dye under conditions tested did not take place. Investigating the influence of Helactine Yellow F5G1 on the activated sludge, the author [11], [12] shows that even with dye dose of 20 mg/dm^3 one can see disturbance in activated sludge activity – the sludge shows considerable reduction in its volume index to a dozen or so cubic centimetres per gram and there are observed formation of 'false sludge' being undecomposed organic culture medium and appearance of microorganisms typical of overloaded sludge. The dye was being adsorbed on the activated sludge but was not biodegraded. The dye showing detrimental effect on the activated sludge appeared to be Chrysophenine G. As early as in the first days of dye dosing, activated sludge mass and volume index decrease. At the dose of dye over 20 mg/dm^3 the sludge activity has considerably been suppressed and the variety of microorganisms has been reduced, too. Despite the fact that forty day adaptation period was applied, biodegradation of the dye did not take place. Quite different results were obtained by the author for Direct Green GB. In the first days of adaptation the dye caused the activated sludge to swell and overflow. After almost thirty days detrimental symptoms disappeared and microscopic examinations proved that the species composition of microflora and microfauna changed. Besides, the research showed that biodegradation of Direct Green GB took place. The author explains considerable diversification of biodegradation of given direct dyes by difference in their chemical structures. The dyes showing detrimental effect on activated sludge were Aniline Orange and Sulfur Brown BR. By applying adaptation process it was possible to adjust the sludge to work in the presence of Aniline Orange in amount of 35 mg/dm^3. However, despite 60-day adaptation its biodegradation did not take place. The Sulfur Brown BR did not decompose in biodegradation process. In summary of her research, the author [12] finds that the activated sludge can be adapted to work in the presence of certain amount of a dye taking, however, advantage of other sources of nourishment. The adaptation period depends on the amount and type of a dye. Biodegradation of some dyes is possible after earlier adaptation of the activated sludge to a dye and this is strictly connected with the type of functional groups of the dye.

Mechanical and biological treatment are applied at the same time. During two-hour sedimentation of textile industry wastewaters in settling tanks one can obtain 40–50% reduction of suspended matter, 15–20% reduction of colour intensity and reduction of

BOD_5 not higher than 8–40%. Filtration and centrifuging may be applied in fat recovery. Centrifuging is a two-stage operation. In the first stage, bigger particles of suspended matter are being separated, and in the second stage liquid fats are being separated. Another method of wool fat separation from wastewaters is its coagulation by means of calcium, aluminium and other salts [2].

Chemical methods include neutralization and oxidation. Commonly used oxidants are chlorine compounds and ozone. Ozone consumption rate depends on wastewater colour intensity and on contents of surface-activated substances. If oxidation proceeds at the same time as biological treatment then the rate of ozone consumption is from 25 to 60 mg/dm^3. Oxidation process carried out with no biological treatment requires ozone consumption rate to be increased up to approx. 120 mg/dm^3 [13]. Investigation carried out on pure solutions of thirty one dyes showed that discolouration rate due to application of ozone depends on the dose of the latter and on the dye contents in a given solution [14]. The process of oxidation also eliminates sulfides from wastewater. As this process proceeds with low rate, authors [15] suggest to apply a manganese salt as catalyst (manganese chloride or sulfate) at Mn^{2+}/S^{2-} ratio of 0.4–0.5 mg/mg with simultaneous aeration of wastewater. Other research works [16] carried out on azo dyes showed that these dyes get oxidized with HOCl and the solution reaction is a decisive factor of the process. The azo dyes can be decomposed by oxidation with hydrogen peroxide in the presence of hydrochloric acid. This process proceeds with the highest rate (from 10 to 12 hours) if hydrochloric acid to hydrogen peroxide ratio is 2:1 [17]. Photocatalytic methods of wastewater oxidation are rather seldom [15], [18].

Among physicochemical methods applied in treating textile industry wastewaters, one ought to mention coagulation, flocculation, coprecipitation, electrolysis, flotation, sorption and others. A known method of treating textile industry wastewaters, post-dyeing in particular, is a German method being carried out in the Niers type reactor. Coagulation of initially acidified wastewater is being carried out by application of an iron salt produced from iron chips. This method, in comparison with a classic coagulation, allows lower acidification of effluent, smaller amount of post-coagulation sediment and full elimination of sulfides. The Niers method has been investigated by Russians [19], [20], [21] who have determined its optimum conditions:

dosage pH	– 2.5–3.0,
contact time	– 30–45 min,
neutralization pH	– 8.5– 9.0,
sedimentation time	– 1.0–1.5 hours.

The coagulation is a simple and commonly applied process. By simultaneous dosing of two coagulants reacting with each other coprecipitation of pollutants proceeds [22]. Research work showed that very good results can be achieved by dosing copper sulfate with calcium hydroxide, whilst maintaining alkaline reaction of wastewater [22]. This process can be carried out with addition of cationic and anionic polyelectrolytes [23]. Firstly, the anionic polyelectrolyte is being added followed by the cationic one. Because of their influence on each other, the undissociated organic complexes are produced; they precipitate in the form of easily sedimenting flocks. As a cationic medium one can add the dyeing fixer IS.

A certain form of coagulation is electrocoagulation, i.e,. electrolysis with iron or aluminium electrodes causing saturation of the solution with Fe^{2+}, Al^{3+} ions to occur. These ions in neutral or slightly alkaline solution form relevant hydroxides. Apart from electrocoagulation some other processes take place at the same time, i.e., electrophoresis, cathode deposits of metals, sludge flotation, as well as ion and molecule sorption on hydroxides. According to [24] the process of electrocoagulation causes suspended matter reduction of 98%, colour intensity reduction by 85%, chemical oxygen demand reduction by 70%, active-surface substances reduction by 90% and the final iron contents in the solution not higher than 0.2 mg/dm^3. The efficiency of wastewater treatment in electrocoagulation process is shown in table 1.

Table 1

Treatment of textile industry wastewaters in the process of coagulation [24]

Indicators	Raw wastewater	Efficiency [%]	
		Pressure flotation	Electro-coagulation
Colour intensity*	1:2 500	40	70
Suspended matter, mg/dm^3	84	64	97
COD, mg O_2/dm^3	12 000	58	75
BOD (full), mg O_2/dm^3	4 600	56	74
Surface-activated substances (SAS), mg/dm^3	550	73	85

*Colour intensity determined by necessary dilution with distilled water to obtain a colourless solution.

The wastewater treatment was being carried out in two stages:

Stage I – with iron electrode.

Stage II – with aluminium electrode.

To protect stability of the coagulation process a flocculant in the amount of 0.5–1.0 mg/dm^3 was being added. In the 1st stage the rate of electricity consumption was 0.73 kWh/m^3 and for the 2nd stage 0.65 kWh/m^3. In the 1st and 2nd stages, the rates of electrode consumption were 80 g Fe^{2+}/m^{3}and 20 g Al^{3+}/m^3.

Disinfection of effluent and increase in pH have taken place during electrolysis [25], [26].

Carrying out the process of electrolysis with a non-corroding titanium electrode covered with isomorphous metal oxide layer with an optional cathode, one can decompose dyes without formation of troublesome sediments [13], [19], [20]. Research work carried out on real wastewater confirmed the efficiency of the method applied – considerable discolouration, reduction of organic substances by 70–80% and surface-activated ones by 75% were secured. However, it should be noted that under optimal conditions adopted by the author [19], [20], i.e., current density – 2 A/dm^2, NaCl concentration – 5 g/dm^3, and reaction time – 10–15 min, strong salinity of effluents have occurred. Research work carried out on model solutions of dyes having the concentrations of 0.2–0.5 g/dm^3 (Acid Direct Orange – KŻ, Direct Brown KH, KS-2K) and chemical and chromatographic analyses of dyes and the products of their electrochemical processing enabled the author [20] to show the final balance of dye decomposition products from which it is evident that dyes in 60–70% decompose with formation of CO_2, N_2, SO_4^{2-} and H_2O. Only 5% of aromatic compounds remain.

NIKIFOROW [13] proposes an electrolytic process with insoluble electrodes to be carried out in the presence of a catalyst in the form of granulated wastes coming from thermal production of manganese dioxide. He [13] has found that during the electrolysis carried out in the presence of the catalyst firstly an intensive mineralization of easily oxidizing organic compounds occurs followed by decomposition of hardly oxidizing substances in the presence of active chlorine. In dynamic system, the electric treatment of wastewater proceeds in wide range of pH variation and with faster rate than during the process of oxidizing wastes by means of chlorine and its compounds. In this process, organic substances can oxidize forming compounds being easily biodegradable or such as H_2O, CO_2, N_2.

Textile industry wastewaters comprising surface-active substances can be treated in flotation and electroflotation processes [10], [27], [28], [29]. The air dispersion flotation is applied with the air consumption rate of 5–6 m^3/m^3 of effluents in a flotation cell being at least 3 metres high. During the process of flotation [29] along with increase in initial concentration of surface-active substances the efficiency of pollutants' reduction increases (including SAS). In this process, the efficiency of nonionic SAS removal is higher than that of the anionic. The assumed period of flotation is 15–45 minutes. Temperature change from 16 to 20 °C has little influence on the foam volume rise rate (5%), whilst with temperature increase from 20 to 40 °C, a 50% foam volume rise rate is obtained. Besides, the solution pH, addition of frothing agents and organic acids contents influence the flotation process efficiency (lowering pH causes decrease of flotability; frothing agents added increase flotability, and organic acid contents lower pH value) [24].

Examples of treatment efficiency of textile industry wastewaters by the air dispersion flotation method have been shown in table 2 (air flow rate: 20–25 m^3/m^2).

Table 2

Flotation of textile industry wastewater with air dispersion [24]

Chemical analysis	Raw effluents	Purified effluents	Efficiency [%]
Colour intensity	1:42	1:25	37
Suspended matter, mg/dm^3	50	30	40
COD, mg O_2/dm^3	400	250	38
BOD (full), mg O_2/dm^3	200	126	37
SAS, mg/dm^3	75	35	55

Another type of flotation is the pressure flotation. In this process, the effluent is being aerated under increased pressure whilst flotation takes place under the normal pressure. The flotation efficiency can be increased by coagulation of wastewater with ferric oxide. The aeration of wastewater in a tank takes two–three minutes under pressure of $3–5\times10^5$ Pa. The volume of air solved should not be higher than 3% and aeration intensity – from 6 to 10 m^3/m^2 hour. The treatment efficiency depends on the wastewater composition and concentration, pressure in aeration and flotation tanks, volume of air, doses of reagents, etc. In table 3, the results of wastewater treatment in the pressure flotation method with addition of aluminium oxide have been shown. For comparison, results for flotation process without coagulant addition have been presented in table 4.

The results of treatment can be improved by application of a several stage flotation [24]. The gas dispersion can be obtained through effluent electrolysis. The gas so evolved can be hydrogen, oxygen, chlorine, carbon monoxide and nitrogen. Such a gas is more active, therefore, the process of flotation with application of it gives better results than normal flotation [24].

Table 3

Pressure flotation of textile industry wastewater with Al_2O_3 coagulation [24]

Chemical analysis	Raw effluents	Purified effluents
Colour intensity	1:500	1:60
Suspended matter, mg/dm^3	220–425	35–50
COD, mg O_2/dm^3	515–710	240–425
BOD (full), mg O_2/dm^3	240–410	145–200

Table 4

Pressure flotation of textile industry wastewater without coagulation [24]

Chemical analysis	Raw effluent	Purified effluent
Suspended matter, mg/dm^3	530	224
COD, mg O_2/dm^3	517	436

Further physicochemical process applied to the treatment of textile industry wastewater is sorption. The following sorbents have been investigated: active carbon, kaolinite, bentonite, gumbrine, coke, cellulose, peat and others [2], [30], [31]. According to LASKOV [32] good effects can be obtained by application of bentonite. It has to be noted that acid dyes adsorb better on loamy materials than normal ones. According to ANIELAK [22] initial treatment of bentonite with hydrochloric or sulfuric acid considerably increases its sorption capacity, therefore its efficiency is important. Researchers from the Brazilian University [33] obtained good results using two different types of active carbon for post-dyeing wastewater treatment. In order to carry out the sorption process properly, a relationship between sorbent and sorbate has to be known [33]. OROZCO [34] used acclimatized plant *Eichhornia crassipes* as sorbent in textile wastewater treatment. The research gave promising results. A 96.6% reduction of colour intensity was observed. Purified effluents were practically colourless. Then, German researchers [35] used for dye adsorption semi-synthetic adsorbents with functional groups in sodium and hydrogen forms received on the basis of zeolite. They adsorbed dyes in a very slight degree (approx. 2–3.5 mg/g of sorbent). Rise of the solution temperature from 20 to 40 °C did not improve the result even with sorption time as long as 150 minutes. Ultrafiltration, electrodialysis and other processes are applied in treating textile industry wastewaters, too [18], [26], [36], [37], [42]. Reduction of toxicity of post-dyeing effluents can be achieved by substitution of strongly toxic synthetic dyes for natural ones, e.g., Indigo commonly used for dyeing jeans clothes. This dye has been substituted for a dye being produced by a plant discovered by American researchers in 1983 [38].

3. TECHNOLOGY OF TEXTILE INDUSTRY WASTEWATER TREATMENT

There are many technological systems of textile industry wastewater treatment applied in practice or proposed for implementation. They differ in sequence, number and type of operations being carried out. The considerable variety of technological systems is often due to changeability of textile industry wastewater composition. Therefore a choice of the technology of effluent treatment should be supported by research activity. Technological systems mentioned below do not fully describe all solutions applied and they only prove the importance of the subject touched.

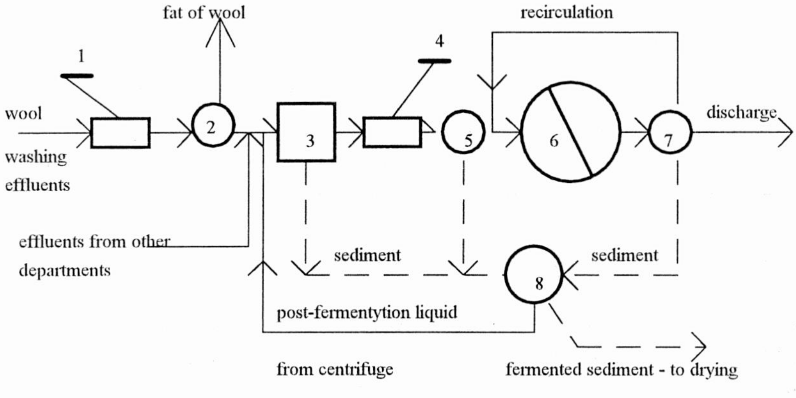

Fig. 1. Diagram showing the treatment of wool industry wastewaters [2]
1 – grit chamber, *2* – fat of wool regeneration device, *3* – surge tank, *4* – coagulation chamber, *5* – initial settling tank, *6* – high-loaded biofilter, *7* – final settling tank, *8* – centrifuge

Some authors suggest application of biofilter [2] in treating wool industry wastewaters. An exemplary technological system with a biofilter has been shown in figure 1. Before effluents are fed to biofilter they have to be averaged in a surge tank. It is recommended to keep them in the tank for 24 hours.

A modernized technological biofilter system for wastewater treatment applied to post-dyeing and domestic sewage has been shown in figure 2. According to the technology developed, initially purified effluents flowing from the biofilter are fed into another one resembling the former. Effluent from the second biofilter is subject to coagulation with aluminium sulfate and Rokrysol WF-2. Moreover, in order to adsorb the remains of the dye, active carbon dust is being added to the effluents.

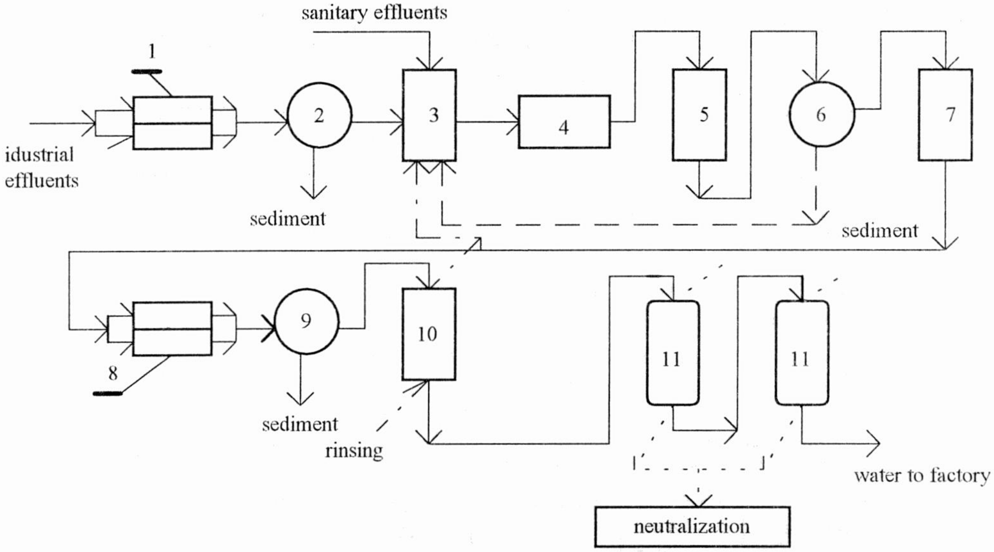

Fig. 2. Diagram showing modernized wastewater treatment plant
– Cooperative R.L. & A. 'Koronka' in Bobowa [11]
1– reaction chamber (oxidation and coagulation), *2* – clarifier, *3* – surge tank, *4* – initial settling tank, *5* – sprinkled bed, *6* – intermediate settling tank, *7* – sprinkling bed, *8* – reaction chamber (coagulation, sorption), *9* – clarifier, *10* – high-rate filter, *11* – ion exchanger

After completion of precipitation process the content of the reaction chamber is being pumped to the clarifier and then to the high-rate filter. Filtrate obtained becomes the water of the 1st class purity. In the case of closed-loop water–effluent system, because of requirements set out for technological water (e.g., hardness of 1.8 mval/dm^3), the filtrate from the high-rate filter is fed into ion exchangers [11], provided that it meets requirements set out for water being fed into ion exchangers [40].

An uncommon technical solution has been proposed for implementation of a treating system in 'WARTEX' Textile Factory in Myszków (figure 3) which is located in a close neighbourhood of a paper mill discharging its post-production effluents after removal of waste cellulose [39]. The idea of treating the post-dyeing wastewaters originates with the concept of their introduction to a mixer and thereafter to centrifuges situated in a paper mill to which the discharge coming from 'DORRA' settling chamber

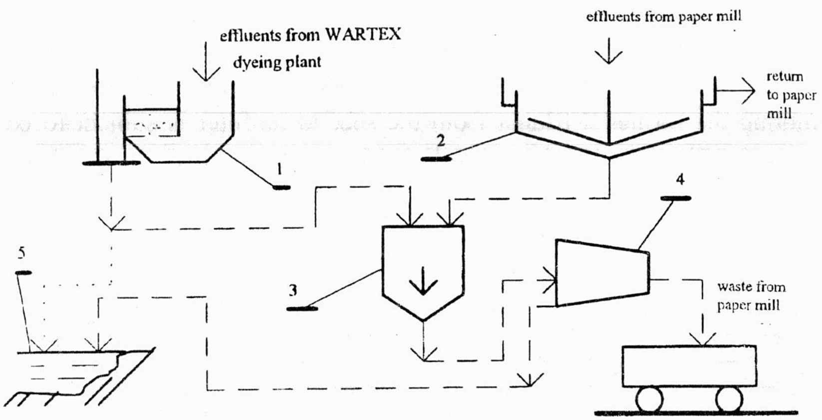

Fig. 3. Post-dyeing wastewater treatment plant – WARTEX textile factory [39]
1 – coke filter, *2* – radial settling chamber type 'DORRA',
3 – mixer, *4* – settling centrifuge, *5* – open tank

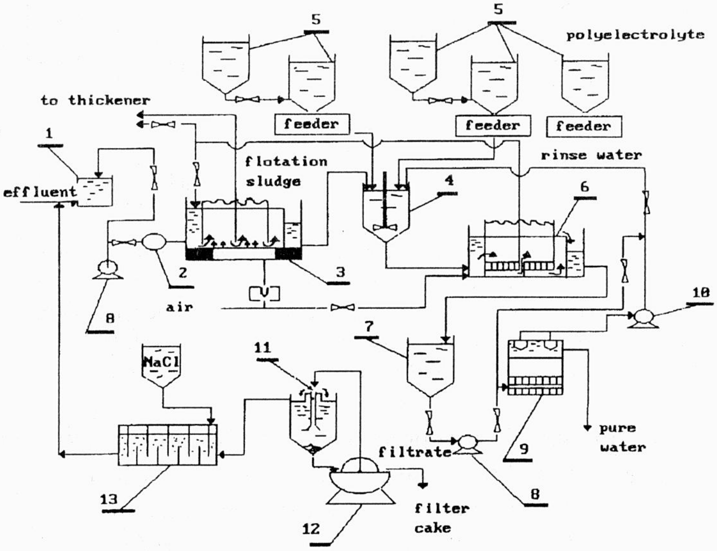

Fig. 4. Technological system of textile wastewater treatment
designed for factories in Ulan-Ude and Klajpeda [10]
1 – averaging tank, *2* – rotameter, *3* – flotation machine, *4* – mixer, *5* – reagent tanks,
6 – electroflotation machine, *7* – tank, *8* – pump, *9* – high-rate filter, *10* – recirculation pump,
11 – condenser, *12* – vacuum filter, *13* – oxidizing electrolysis chamber

containing waste cellulose should be directed. In the above mentioned mixer, both effluents coming from 'WARTEX' and paper mill are being mixed for a dozen or so minutes and then dehydrated in settling centrifuges.

Laboratory tests showed that with addition of active carbon (approx. 5%) full discolouration of effluent can be achieved (100% light transmission at λ ranging from 185 to 205 nm).

A system shown in figure 4 has been designed for knitted fabric factories in Ulan-Ude and Klajpeda. This makes possible reduction of suspended matter by 99%, dyes contents by 85% and SAS by 90% [10]. In this system, open flotation machines are suggested to be applied as they provide, according to investigations being carried out, reduction of colour intensity by 30% and that of COD by 26%. By application of a several stage flotation, the results of treatment can be enhanced yielding SAS reduction by 50–60%, colour intensity reduction by 40% and COD – by 35%. Additionally, an electroflotation machine has been introduced to wastewater treatment process. The flotation sludge gets concentrated in a settling tank and dehydrated in a vacuum filter.

The filtrate together with the settling tank overflow are fed into the electrolysis chamber equipped with graphite electrodes where a temperature range of 40–50 °C is suggested to be maintained in order not to damage the electrodes.

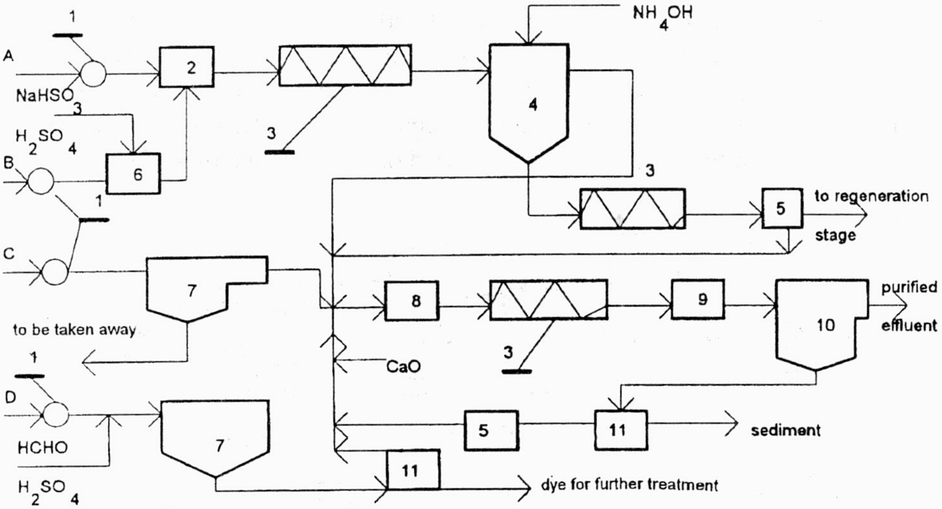

Fig. 5. Treatment of wool industry wastewater containing high amount of solids and surface-active agents with simultaneous recovery of the dye [5]
1 – mesh sieve, *2* – mixer, *3* – heat exchanger, *4* – settling chamber, *5* – centrifugal separator, *6* – reaction chamber, *7* – sand/grease removing tank, *8* – averaging tank, *9* – pressure tank, *10* – flotation chamber, *11*– centrifuge, *12* – condensing settling chamber, *A* – tanning effluents, *B* – staining effluents, *C* – washing effluents, *D* – post-dyeing effluents

For wool industry wastewater treatment Russians [5] suggest a technological system shown in figure 5. This technology has been developed for wastewaters containing high amounts of solids, surface-active substances (from 1 to 1.5 g/dm^3), NaCl (up to 20 g/dm^3), dyes (up to 6 g/dm^3), hexa- and trivalent chromium and other substances like formaldehyde and fats.

According to the method developed the wastewater is filtered through 2.5–3 mm mesh sieves. Then fine fibre, hair, fat and sand are removed in sand/grease removing tanks. Thereafter the wastewater is fed into a surge tank equipped with a pneumatic stirrer (mixing rate is approximately 10 m^3/m^3, time – from 6 to 8 hours). Wastewater comprising hexavalent chromium before being fed into the averaging tank is subject to reduction in acid reaction to trivalent chromium which is, subsequently, precipitated in the form of chromium hydroxide by adding calcium hydroxide.

Wastewaters containing dyes in the amount of 3–5 g/dm^3 are proposed to be subject to dye recovery process by application of the formaldehyde method. Sediment formed is being separated in a centrifuge and the solution having its final colour determined by the degree of dilution ranging from 1:100 to 1:200 is being fed to a surge tank. Averaged wastewater is filtered through sieves and then is subject to pressure flotation being carried out with a 50% recirculation of the solution.

The post-flotation sludge is dehydrated in centrifuges. The centrifuge filtrate is further purified in separators. Pretreated wastewater shows decrease of the following parameters: colour – by 90–95%, suspended matter – by 80–90%, COD by 75–80% and fat – by 95%. The effluents are still loaded with salt and it is suggested that they be further purified by ultrafiltration. It is a complex and energy-consuming system.

The textile industry wastewaters can be treated in a reactor for chemical pollutant decomposition (Niers method) according to technological system [41] as shown in figure 6 or by means of biological treatment carried out at the same time [2].

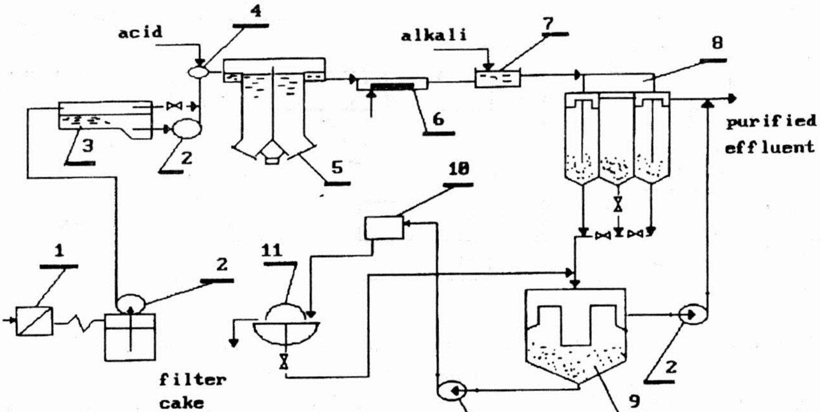

Fig. 6. Treatment system of textile wastewater with a reactor for chemical decomposition of dyes [41]
1 – fibre trap, *2* – pump, *3* – averaging tank, *4* – mixer, *5* – reactor, *6* – degasifier, *7* – alkali mixer, *8* – clarifier, *9* – sludge thickener, *10* – sludge feeder, *11* – vacuum filter

Some authors [33], [43], [44], [45] think that textile industry wastewaters should be treated simultaneously with other effluents, domestic sewage in particular, which will facilitate selection of proper and most favourable way of their treatment on the grounds of full factor-economic analysis.

4. RECAPITULATION

Various technological systems are being used for the treatment of post-dyeing wastewater. In most cases, the wastewater is subject to many operations. The following methods are being used: mechanical, chemical, physicochemical and biological ones. Each of the methods mentioned therein enables a decrease in the concentration of substances contained in wastewater to occur. Many year practice in the treatment of post-dyeing wastewaters in municipal sewage treatment plants shows that after biological treatment the post-dyeing effluents often do not change their colour or discolour insignificantly. At the same time investigations have shown that there are admissible concentrations of those dyes at which effluents can be successfully treated biologically. Therefore, one should say that partial or complete removal of dyes is necessary before biological treatment of effluents. This can be achieved by application of simple physicochemical methods, e.g., coprecipitation and sorption, or those requiring special apparatus to be used like electrolysis, electrodialysis, flotation and ultrafiltration. The author's long-term cooperation with managers of many textile factories indicates that they are interested in simple technological systems where coagulation, sorption and sedimentation are mostly applied. Unfortunately, coagulation quite often gives different results, depending on the wastewater composition and also on other methods applied in the same time as coagulation.

Investigations made on real effluents show that dyes can precipitate due to application of coagulation carried out with two reagents, i.e., salt and calcium hydroxide. It is a cheap and simple method. Full removal of dyes can be achieved as the result of simultaneous application of sorption and coagulation. Real wastewaters tested so far contained casual dyes. Therefore, it is advisable to carry out some model research involving a big group of various dye solutions which will enable a precise interpretation and optimization of the process to be achieved.

Assumptions and plan of the research work to be carried out. Coagulation, which is a process of agglomeration of solid particles, is strictly connected with the electrokinetic potential. Particles of colloidal suspension having high electrokinetic potential and the same polarity will be subject to electrostatic repulsion and coagulation of these particles will not take place. However, for the solid particles having different polarity surface charges in water solution, autocoagulation will take place due to electrostatic attraction. Thus, the decrease of surface or electrokinetic potential will result in the decrease of electrostatic repulsion forces and facilitate formation of flocks and their sedimentation.

Having analysed the chemical composition of dyes used for fibre colouring one can find that these are mostly organic compounds of developed structure. They are hydrocarbons with quinoid configuration, chromophores and auxochromes.

The presence of a chromophore is necessary (although mostly not sufficient) for a colour to exist. The chromophores have mobile groups of electrons ,i.e., they form a system where delocalization of electrons occurs easily. This causes that light absorption is shifted towards longer wavelength, namely, the visible part of the spectrum.

Auxochromes, $-CH_3$, $-NH_2$, $-SO_2NH_2$, facilitate formation of a electropositive ion, whilst such anti-auxochromes (name after Witzinger) as $-SO_3Na$, $-OH$, $-NO_2$ facilitate formation of an electronegative ion. Dyes, depending on their type, are being applied in the form of aqueous solutions or in the form of aqueous solution saturated with sodium chloride or aluminium sulfate forming on a fabric trivalent metal compounds (aluminium, iron, chromium). It can be assumed that dosing a coagulant to the dye solution results in adsorption of coagulant cation on the anionic functional group of the dye (acid or weak acid) or a donor–acceptor complex with the dye chromofore, its functional group and metal ion will be formed. Iron salt added to the dye solution hydrolyses to form a hydroxide (ferrous or ferric, depending on the oxidation state of iron) insoluble in water. The trivalent iron salt hydrolyses by stages according to the following reactions:

$$[Fe(H_2O)_6]^{3+} + H_2O = [Fe(H_2O)_5OH]^{2+} + H_3O^+, \tag{4}$$

$$[Fe(H_2O)_5(OH)]^{2+} + H_2O = [Fe(H_2O)_4(OH)_2]^{+} + H_3O^+, \tag{5}$$

$$[Fe(H_2O)_4(OH)_2]^{+} + H_2O = [Fe(H_2O)_3(OH)_3] + H_3O^+ = Fe(OH)_3 + 3H_2O + H_3O^+. \tag{6}$$

The iron hydrocomplexes produced form an adsorption surface for dyes and its general surface potential changes depending on the solution reaction. The surplus of positive charges occurring at acid reaction decreases with this reaction increase up to zero in neutral medium. With the increase of OH^- ion concentration negative hydrocomplexes like:

$$[Fe(H_2O)_2(OH)_4]^{-},\ [Fe(H_2O)(OH)_5]^{2-},\ [Fe(OH)_6]^{3-} \tag{7}$$

should appear.

Most dyes have sulfone functional groups dissociating in a full range of reaction change. The dyes are adsorbed with those functional groups to a positively charged surface by electrostatic attraction. Other functional groups will dissociate, depending on the medium reaction. The following model of dyes sorption onto hydrocomplex surfaces can be adopted:

$$\begin{gathered}\left[\frac{\left(\mathrm{B}-\mathrm{SO}_3^-\right)^+}{\left(\mathrm{B}-\mathrm{SO}_3^-\right)^+}\left(\mathrm{Fe}\left(\mathrm{H}_2\mathrm{O}\right)_5\mathrm{OH}\right)\right]\\[2em]\left[\frac{\left(\mathrm{B}-\mathrm{SO}_3^-\right)^+}{\left(\mathrm{B}-\mathrm{SO}_3^-\right)^+}\left(\mathrm{Fe}\left(\mathrm{H}_2\mathrm{O}\right)_6\right)^+\right]\end{gathered}\tag{8}$$

According to the author it must be assumed that the donor–acceptor complexes of dyes with metal ion formed previously will produce unstable hydrocomplexes. From the above analysis it is evident that in alkali medium, where iron hydroxides have negative surface potential, no adsorption of dyes having negative molecule potential should take place. However, by adding iron salt in the first stage we can obtain iron–dye complexes having positive potential which can easily be adsorbed on a hydroxide surface (ferrous, ferric, calcium).

Electrostatic sorption in neutral medium, where hydrocomplexes have zero surface potential, should not take place.

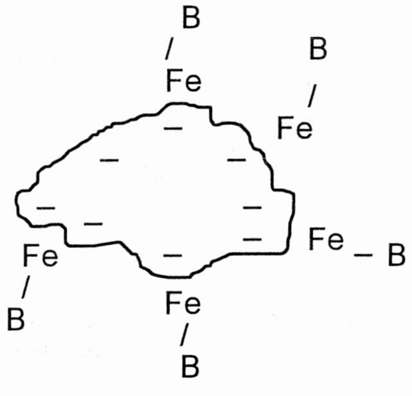

Fig. 7. Adsorption of dye B with participation of iron ions Fe^{n+} on a sorbent having negative surface potential

Sorption capacity of hydrocomplexes is limited. Unsaturated iron ions will be left in the solution as well as unadsorbed iron-complexes of the dye with iron ions. In order to eliminate the dye and iron ions from the solution one can add thereto an alkali, thus increasing alkalinity of the solution or introduce a sorbent having negative surface potential. Iron ions should be adsorbed to such a sorbent surface. The sorbent surface should acquire surplus of positive charge with proper iron concentration. On the surface modified in such a way there are created proper conditions for adsorption of the dye left in the solution or, alternatively, the unmodified sorbent will adsorb complexes of the dye with iron ions (figure 7). Under properly selected conditions (like the relevant amounts of salt and sorbent in relation to dye concentration and proper pH) one should achieve full removal of dye from solution. In order to verify the above assumption, a research according to the following plan has been adopted:

1. Selection of coagulants and sorbent.
2. Potential measurements of sorbent and sediment precipitated.
3. Investigation of precipitation process.
4. Investigation of sorption process.
5. Investigation of precipitation and sorption as two processes that occur subsequently one after another.

Having achieved positive results, a technology of post-dyeing wastewater treatment with application of coprecipitation and sorption will be developed.

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USUWANIE WŁÓKIENNICZYCH ŚCIEKÓW PRZEMYSŁOWYCH

Artykuł stanowi przegląd dotychczas opublikowanych prac na temat oczyszczania ścieków włókienniczych za pomocą metod mechanicznych, fizykochemicznych, chemicznych i biologicznych. Opisano również działające systemy technologiczne, które zaproponowano do oczyszczania włókienniczych ścieków przemysłowych. Na podstawie wyników otrzymanych przez różnych badaczy zarekomendowano użycie prostej metody oczyszczania ścieków pofarbiarskich. Metoda ta może być stosowana do usuwania wszystkich barwników, a jej skuteczność potwierdza analiza zjawisk zachodzących podczas oczyszczania dokonana przez autorkę tego artykułu.